PHYSICAL AND ELECTROCHEMICAL CHARACTERIZATION OF CATALYSTS FOR OXYGEN REDUCTION IN FUEL CELLS

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Introduction

In low temperature fuel cells the oxygen reduction reaction (ORR) at the cathode is responsible for a large part of the losses of the conversion from chemical to electrical energy. Especially for the reaction kinetics the catalyst is the crucial factor, while the structure of the electrodes is important for catalyst utilization, efficient mass transport and durability of the cell. In particular, the cathode catalysts currently used are associated with major cell efficiency losses, because of the kinetic limitation of the oxygen reduction reaction.
To solve this problem a better understanding of the key steps in the oxygen reduction process on commonly used cathode catalysts as well as of alternative catalysts is required. For this purpose physical and electrochemical methods are used to characterize the catalysts. Besides the V-i-characteristics and the electrochemical impedance spectroscopy (EIS) as electrochemical methods, the physical methods porosimetry by mercury intrusion and temperature programmed reduction (TPR) are used to characterize the catalysts. Additionally, surface science analytical methods such as x-ray photoelectron spectroscopy (XPS) provide important insights into the structural and chemical properties of the catalyst. In order to perform a complete surface science analysis of the catalysts it is not sufficient to investigate freshly prepared catalysts, but also necessary to study the catalysts after operation in fuel cells or after electrochemical treatment. Comparing the catalysts before and after the electrochemical stressing the alterations of the catalysts can be determined.
As an example the results of combined investigations of carbon supported ruthenium-selenide cathode catalysts operated in a DMFC are presented here.

Carbon supported RuSe- catalysts

Following catalysts are compared:

- 40 wt% RuSe/C (26.0 wt.% Ru, 13.4 wt.% Se) (TUM)
- 20 wt% RuSe/C (18.7 wt.% Ru, 0.9 wt.% Se) (HMI)
- 40 wt% Pt/C (Reference catalyst)

Physical characterization

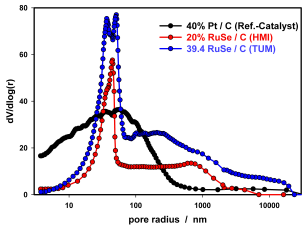

Fig. 1: Pore size distribution of carbon supported catalysts with RuSe and Pt (by Hg-porosimetry)

RuSe/C catalysts have a pore system at 30 – 50nm, that is mainly dominated by the carbon support (Vulcan XC72).

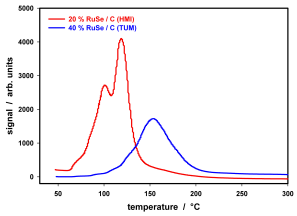

Fig. 2: TPR-spectra of RuSe/C catalysts (reduction temperature:
20 wt% Ruse/C: 120°C;
40 wt% RuSe/C: 154°C)

Higher reduction temperature of 40 wt.% RuSe/C catalyst is caused by the higher Se to Ru ratio (a more stable oxide).

Electrochemical characterization

Single cell tests of RuSe/C DMFC cathodes

Catalyst and metal content	Metal loading, content of electrolyte
Anode: PtRu black (JM)	1.00 mg_{PtRu}/cm^2 + 30 wt.% Nafion
Cathode: 40 wt.% Pt/C (Ref.-catalyst)	0.10 mg_{Pt}/cm^2 + 20 wt.% PTFE
20 wt.% RuSe/C (HMI)	0.14 mg_{RuSe}/cm^2 + 20 wt.% PTFE
40 wt.% RuSe/C (TUM)	0.13 mg_{RuSe}/cm^2 + 20 wt.% PTFE
Membrane	Nafion 117
GDL	E-Tek single sided ELAT V3
Active area ; single meander flow field	23 cm^2
MEAs prepared with DLR Dry Spraying Technique	
MEAs were not prepared with the DLR standard loading for the DMFC, which is: 1.6 mg/cm^2 for the anode (PtRu) and for the cathode (Pt). The prepared electrodes were very thin and the catalyst loading was too low. These may be the main reasons for the low cell performance measured in the DMFC.	

Standard operating conditions in DMFC mode	{optimized conditions of RuSe/C}
Anode flow rate: CH_3OH (1.5 mol/l) (pressure: 2.5 bar)	{5 ml/min} 10 ml/min
Cathode flow rate: O_2 (pressure 3.0 bar)	{60sccm, 180sccm} 600sccm

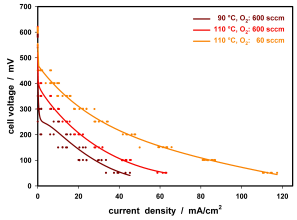

Fig. 3: V-i characteristics of MEA with 20 wt.% RuSe/C cathode catalyst, variation of cathode flow

Increase of the cell temperature and a lower oxygen flow rate lead to an increase of the cell performance. RuSe/C catalysts allow a higher water content in the cathode. This indicates a different hydrophobic character compared to Pt catalyst or an improved water transport.

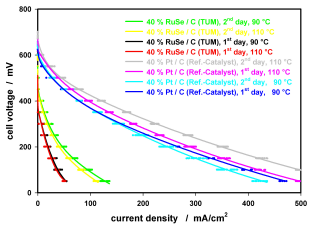

Fig. 4: Change of V-i characteristics from 1st to 2nd day

The general increase of cell performance from 1st to 2nd day for RuSe/C catalyst is caused by an improved water balance. In contrast, the performance of the MEA with the Pt catalyst is increased at 110°C, whereas the performance at 90°C is decreased. This behavior of the MEAs with the Pt and with the RuSe catalysts indicates that the catalysts have significantly different hydrophobic properties.

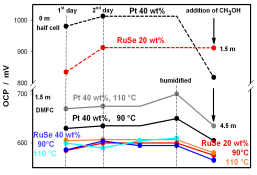

Fig. 5: Open circuit potential (OCP) measured for the Pt and the RuSe cathode in half cell configuration (1m:=mol/l H_2SO_4) and open cell voltage measured in the DMFC

OCP of MEA with RuSe catalyst is lower compared to Pt catalyst. Voltage drop for RuSe due to increased CH_3OH concentration indicates an anodic effect. The anode reaction must also be influenced by the different cathode catalysts, maybe by the formation of H_2O_2 on the cathode, which can crossover the membrane to the anode, where a mixed potential can be formed.

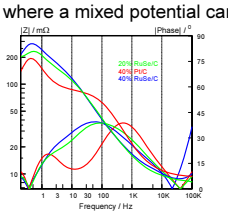

Fig. 6: Bode-diagram of the EIS measured at 800 mA, 90°C, 1.5 mol/l MeHO

The cell with 40 wt% Pt/C cathode shows the highest catalytic activity. Electrode with 20 wt% RuSe/C has a higher catalytic activity compared to the 40 wt% RuSe/C cathode. Minor differences in the high-frequency range of the diagram are caused by a different conductivity of the electrode material.

Physical characterization – post mortem

XPS investigation of RuSe/C catalysts before and after the electrochemical stressing

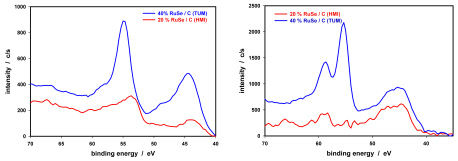

Fig. 7: Se 3d (and Ru 4p) spectra of new (right) and electrochemically stressed (left) electrodes with RuSe/C catalyst

Increase of Se 3d peak of 20 wt% RuSe/C catalyst after operation indicates cleaning effect. Se is present in two forms: as selenides and in oxidized form. Significant decrease of the selenium oxide peak of 40 wt.% RuSe/C catalyst was measured after stressing.

Conclusions

The application of the selected methods for physical and electrochemical characterization leads to useful results for further development of new catalyst systems.

- Catalyst composition and MEA structure change due to electrochemical stressing (DMFC and XPS measurements)
- Reaction kinetics of Pt and RuSe cathodes are different (as deduced from EIS measurements)
- Methanol tolerance of RuSe catalysts is confirmed, increased methanol concentrations affect Pt anodes (OCP in DMFC and half cell experiments)
- Surface composition of catalysts depends on support and preparation (XPS, Hg-porosimetry)

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